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PTILOLITE FROM UTAH

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INTRODUCTION

A pink radial mineral from Coyote, Garfield County, Utah, was received for identification some years ago from Hoyt S. Gale, at that time a member of the United States Geological Survey. Mr. Gale had received the specimen from Professor George T. Henry of Marysvale, Utah. While resembling a zeolite in appearance, its properties were not those of zeolites, and a chemical analysis suggested either mordenite or ptilolite. A study of the mordenite-ptilolite group was thereupon undertaken and, as described in the following paper, it was found that these two minerals are very closely related and have been mistaken for each other in the past, but are distinct with individual properties. According to the conclusion reached, the pink mineral from Utah is ptilolite.

The specimen has the character of an amygdaloidal filling in basalt and measures about 7 by 4 by 3 centimeters. The greater part of the specimen is composed of radial groups or imperfect half-spherulites of pink needles about a centimeter long. The centers of these half-spherulites lie close to the surface of the specimen; the space between the two layers of half-spherulites is filled with coarsely cleavable calcite.

DESCRIPTION OF CRYSTALS

The ends of the pink needle-like crystals are completely imbedded in the calcite. On dissolving the carbonate with acid, the radiating needles of ptilolite are exposed, many of them showing terminal faces. Some of the individual prismatic crystals are of equal thickness and others are somewhat flattened, resembling a yard stick in shape. They show a good cleavage in the prism zone and the individual pieces are more of a prismatic columnar shape than a finely fibrous one. The crystals exhibit a tendency to split into several fibers at the attached end. The thickness of the larger individual crystals averages about 0.06 millimeters, though many

of them are almost hair-like. The color is pink, similar to the red-dish color of many heulandites though not so intense. Scattered through the pink fibrous cores are streaks where the ptilolite is colorless, yellowish, or pale greenish. The luster of the larger prisms is vitreous, that of the radiating fibrous masses, satiny.

Although many of the crystals freed from the calcite matrix are terminated, such faces are very minute and uneven and though brilliant, yield a mass of very poor and indistinct reflections on the goniometer. The prism zone is strongly striated, vertically, many of the crystals giving an almost continuous band of reflections, with a maximum brightness for the position of the faces.

The crystal forms present are: $c(001)$, $b(010)$, $a(100)$, $m(110)$, and $o(101)$. All of these forms have been previously noted, $c(001)$ by Cross and Eakins,¹ Colomba, and Grattarola, and $o(101)$ by Grattarola, D'Achiardi, and Bøggild; the latter also found the pyramid $p(111)$.

The axial ratio given by Bøggild, namely $a:b:c=0.8785:1:0.3606$, is adopted, even though his prism angle ($a \wedge m=41^\circ 18'$) is based on measurements of flokite, which as shown in the following paper, is identical with mordenite and not with ptilolite. The prism angle of the two species is apparently very similar and as the angle given is the only one available it is here used.

The measurements on the crystals of ptilolite from Utah are shown below.

MEASUREMENTS OF PTILOLITE FROM UTAH

Form	Measured		Calculated	
	ϕ	ρ	ϕ	ρ
	° /	° /	° /	° /
$c(001)$	4±	0 00
$b(010)$	0 14	90 00	0 00	90 00
$a(100)$	89 59	90 00	90 00	90 00
$m(110)$	47 50	90 00	48 42	90 00
$o(101)$	90 04	22 35	90 00	22 49
$p(111)$	48 42	29 15

The faces of $c(001)$ are very minute specks, giving no reflections. No crystal was observed on which both $c(001)$ and $o(101)$ are present.

¹ For references, see literature cited in the following paper.

The three forms of the prism zone vary in size, even on the same crystal. The two pinacoids, in general, seem to be larger than the prism faces. All three forms are strongly striated vertically.

The macrodome $o(101)$ is the only termination on several of the crystals and seems to be characteristic of the termination of ptilolite. The faces are somewhat elongated parallel to the b -axis.

OPTICAL PROPERTIES

The minute crystals all show strictly parallel extinction on all faces in the prism zone. A faint birefringence could be readily detected on the larger crystals if purposely placed as little as 2 degrees out of parallelism with the cross-hairs of the microscope. Ptilolite is definitely orthorhombic. The elongation of the crystals is negative. The optical orientation could not be determined further than that the axial plane is parallel to the elongation. The refractive indices are: α (parallel elongation) = 1.473, β = 1.475, γ (normal elongation) = 1.478.

CHEMICAL COMPOSITION

The minute crystals of ptilolite fuse quietly and fairly readily to an opaque white enamel. Aggregates of crystals, when fused, show a slight intumescence. The mineral is insoluble in hydrochloric acid, even on boiling.

The analysis of the mineral, freed from calcite, shows it to have the following composition.

ANALYSIS AND RATIOS OF PTILOLITE FROM COYOTE, GARFIELD COUNTY, UTAH

	Analysis	Ratios	
SiO ₂	67.35	1.1206	10.04 or 10
Al ₂ O ₃	11.49	.1126	1.01 or 1
CaO.....	3.87	.0690	} .1126
K ₂ O.....	0.11	.0012	
Na ₂ O.....	2.63	.0424	
H ₂ O—.....	5.13	} .7750	6.94 or 7
H ₂ O+.....	8.82		
	99.40		

The ratios of the analysis, grouping CaO, K₂O, and Na₂O, together, show that the formula of the mineral is 10 SiO₂ · Al₂O₃ · (Ca, K₂, Na₂) O · 7 H₂O.

THE MORDENITE-PTILOLITE GROUP; CLINOPTILOLITE, A NEW SPECIES

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INTRODUCTION

The preceding description of ptilolite from Utah, confirms previous determinations of its orthorhombic character and shows its formula to be $10\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{RO} \cdot 7\text{H}_2\text{O}$. The analyses of mordenite, as given in the literature, show a very similar composition, but optical examination shows its fibers to have a small but definite inclined extinction. Grouping all the available analyses of mordenite, ptilolite, and related minerals (flokite), as far as possible, into two groups, depending on whether the material has parallel or inclined extinction, has shown that there are three distinct minerals, very similar in their properties.

Conflicting statements as to their relationships have been published; thus Bøggild¹ has urged the identity of flokite (shown to be mordenite) with ptilolite, and Walker the identity of ptilolite with mordenite. By correlating the published data as to composition, crystallography, and optical properties, supplemented by new determinations, it is shown that three distinct species are represented by these high-silica, acid-insoluble, zeolite-resembling minerals:

1. Mordenite (How, 1864), $9\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot (\text{Ca}, \text{K}_2, \text{Na}_2) \text{O} \cdot 6\text{H}_2\text{O}$. Monoclinic or triclinic, with inclined extinction of about 5° .

2. Ptilolite (Cross and Eakins, 1886), $10\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot (\text{Ca}, \text{K}_2, \text{Na}_2) \text{O} \cdot 7\text{H}_2\text{O}$. Orthorhombic, with parallel extinction.

3. Clinoptilolite. The mineral from Wyoming described by Pirsson in 1890 and accepted by Dana (6th ed.) as crystallized mordenite. It is evidently a dimorphous form of ptilolite, $10\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot (\text{Ca}, \text{K}_2, \text{Na}_2) \text{O} \cdot 7\text{H}_2\text{O}$, but is monoclinic, tabular and not fibrous, with large extinction angles. It is proposed to rename this mineral from Wyoming, *clinoptilolite*, referring to its inclined extinction but agreement in chemical composition with ptilolite.²

Thugutt arrived at similar conclusions, regarding ptilolite with parallel extinction as having a 10:1 silica-alumina ratio, with the formula $10\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot (\text{Ca}, \text{Na}_2, \text{K}_2) \text{O} \cdot 6 \frac{2}{3} \text{H}_2\text{O}$, the formula given in Dana for mordenite. He also recognized that mordenite, with a similar formula, had inclined extinction.

¹ See bibliography at end of paper for references.

² These conclusions have been reported in *The American Mineralogist*, vol. 8, pp. 93-94, 1923.

DISCUSSION OF ANALYSES

If the analyses of mordenite and of ptilolite, as given in the literature, be grouped into one of two classes, depending on whether the mineral has parallel or inclined extinction, and the ratios calculated from the analyses, it will be found that those having inclined extinction agree with the formula $9\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{RO} \cdot 6\text{H}_2\text{O}$ (mordenite), and those with parallel extinction agree with the formula $10\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{RO} \cdot 7\text{H}_2\text{O}$ (ptilolite), with the exception of the mineral from Wyoming, described by Pirsson, and here called clinoptilolite.

Grouping all the analyses, according to their ratios, under one or the other of the two formulas given, the analyses of mordenite are as follows:

ANALYSES OF MORDENITE

Number	1	2	3	4	5	6	7	8	9
Locality	Nova Scotia	Tyrol	Iceland	Nova Scotia	Nova Scotia	Idaho			
Biblio. ref.	How 1	Thugutt 9	Callisen 10	Walker & Parsons 14	Walker & Parsons 15	Ross & Shannon 16			
SiO ₂	68.40	66.86	67.69	67.08	67.18	64.84	65.88	67.24	66.25
Al ₂ O ₃	12.77	12.13	12.43	11.85	12.36	12.07	12.40	12.94	11.88
CaO.....	3.46	3.86	2.65	1.56	3.42	3.08	3.52	2.72	2.75
Na ₂ O.....	2.19	2.41	4.36	4.74	3.34	3.80	3.52	4.08	4.05
K ₂ O.....	0.16	0.67	2.08	0.47	0.38	0.56	0.36	0.69
H ₂ O.....	13.02	13.87	13.35	12.84	13.23	14.79	13.40	13.44	13.85
Fe ₂ O ₃	0.03	0.31	0.24
MgO.....	0.17	0.09	0.26	0.48	0.28	0.44
Total.....	100.00	100.00	100.57	100.46	100.24	99.22	99.76	101.06	99.91
Extinction.	Small ^a	7°-8°	5°	Small ^a	—	3°40'	Small	—	—

^a Determined by the writer.

The second analysis given by Walker and Parsons (Biblio. 14) is omitted as the sample contained "small spherical radiations of some other zeolite."

The ratios calculated from these analyses are given below, combining CaO, Na₂O, and K₂O into RO. In obtaining the figures, a weighted average is taken for each analysis, instead of arbitrarily taking any constituent as unity. A glance at the figures reveals not only a very close similarity for each constituent in the different analyses but shows very close agreement with the formula $9\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{RO} \cdot 6\text{H}_2\text{O}$.

RATIOS OF ANALYSES OF MORDENITE

Number	1	2	3	4	5	6	7	8	9	Av.
SiO ₂	9.30 9×1.03	8.87 9×0.99	9.06 9×1.01	9.11 9×1.01	9.06 9×1.01	8.53 9×0.95	8.86 9×0.98	8.96 9×1.00	8.83 9×0.98	8.95 9×0.99
Al ₂ O ₃	1.02	0.95	0.98	0.95	0.98	0.94	0.98	1.02	0.93	0.97
RO.....	0.81	0.95	0.96	1.03	0.98	1.00	1.12	1.01	1.07	0.99
H ₂ O.....	5.93 6×0.99	6.17 6×1.03	5.98 6×1.00	5.85 6×0.97	5.98 6×1.00	6.52 6×1.09	6.03 6×1.01	6.00 6×1.00	6.17 6×1.03	6.07 6×1.01

The analyses of ptilolite, with a 10:1 ratio of SiO₂ to Al₂O₃, are as follows:

ANALYSES OF PTILOLITE

Number	10	11	12	13	14	15	16	17	18
Locality	Custer County, Colorado	Jefferson County, Colorado	Crown Prince Rudolph Island	Elba	Iceland	Faroer Islands	Faroer Islands	Guadalcanar	Utah
Biblio. ref.	Cross and Eakins 2	Cross and Eakins 4	Colomba 6	D'Achiaridi 7	Lindström 8	Thugutt 9	Thugutt 9	Tschermak 12	Schaller 17
SiO ₂	67.83	70.35	67.52	65.21	67.15	78.70	74.34	67.23	67.35
Al ₂ O ₃	11.44	11.90	10.76	11.20	11.63	7.22	8.84	10.92	11.49
CaO.....	3.30	3.87	3.31	3.77	2.33	1.99	2.18	1.83	3.87
Na ₂ O.....	2.63	0.77	1.19	{ 6.07 14.22	4.46	2.08	2.74	3.92	2.63
K ₂ O.....	0.64	2.83	1.69		0.72	0.30	0.43	0.58	0.11
H ₂ O.....	13.44	10.18 ^a	14.43		13.98	9.71	12.05	14.91	13.95
Fe ₂ O ₃	0.09	tr.	0.29
MgO.....	tr.	tr.	0.34
Total.....	99.28	99.90	98.90	100.47	100.36	100.00	100.58	100.02	99.40
Extinction.	0°	0° ^b	0°	0°	0° ^b	0°

^a See footnote under table showing ratios.

^b Determined by the writer.

The ratios calculated for these analyses are as follows:

RATIOS OF ANALYSES OF PTILOLITE

	10	11	12	13	14	15	16	17	18	Av.
SiO ₂	10.23 10×1.02	10.06 10×1.01	10.00 10×1.00	9.83 10×0.98	9.95 10×1.00	(*)	(*)	9.78 10×0.98	10.04 10×1.00	9.98 10×1.00
Al ₂ O ₃	1.02	1.00	0.94	1.00	1.02	0.93	0.91	0.94	1.01	0.97
RO	0.98	0.97	0.86	1.09	0.95	0.94	0.96	1.01	0.97
H ₂ O	6.79 7×0.97	4.88 ^b	7.16 7×1.02	7.18 7×1.03	6.94 7×0.99	7.11 7×1.02	7.12 7×1.02	7.26 7×1.04	6.94 7×0.99	7.06 7×1.01

* Ratios not given as sample analyzed was mixed with silica.

^b The ratio of the water is low. The authors state that "The mineral began to lose water at a very low temperature and even on drying in the air bath at 100°C. there was a noticeable loss; the amount thus lost, however, was found to be regained upon exposure to the air, and before the analysis was made the material was allowed to remain loosely covered for several days." The sample was analyzed in the "very dry" climate of Denver. The authors suggest that the Denver climate "may have had sufficient desiccating power to remove part of the water from the mineral analyzed there."

The ratios are in very close agreement with the formula $10\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot (\text{Ca}, \text{Na}_2, \text{K}_2)\text{O} \cdot 7\text{H}_2\text{O}$.

The distribution of the CaO, Na₂O, K₂O, and MgO, as given in the analyses, which have been grouped together as RO, on the basis of ratio percentages, is as follows, given with decreasing CaO.

The table shows that there is no distinction in the distribution of the RO bases between mordenite and ptilolite. CaO is 50 per cent or over in 3 mordenites and 4 ptilolites; Na₂O is 50 per cent or over in 4 mordenites and 2 ptilolites. In both of these minerals, CaO and Na₂O seem to be mutually replaceable to almost any extent. In no analysis, is K₂O over $33\frac{1}{3}$ per cent. In the single analysis of clinoptilolite, the CaO, Na₂O, and K₂O are present in the ratio of 1:1:1.

PERCENTAGE OF BASES GROUPED AS RO, WITH DECREASING CaO

Analysis No.	Mordenite	Ptilolite	CaO	Na ₂ O	K ₂ O	MgO
11	..	P	62	11	27	..
12	..	P	62	20	18	..
1	M	..	62	35	3	0
18	..	P	61	38	1	..
2	M	..	58	33	6	3
10	..	P	55	39	6	..
5	M	..	51	45	4	..
15	..	P	49	47	4	..
7	M	..	46	41	4	9
6	M	..	44	48	3	5
16	..	P	44	51	5	..
3	M	..	40	58	..	2
8	M	..	39	52	3	6
9	M	..	37	50	5	8
14	..	P	35	59	6	..
^a 19	^a	^a	31	32	33	4
17	..	P	30	58	5	7
4	M	..	22	60	18	..

^a Clinoptilolite from Wyoming.

CLINOPTILOLITE

The clinoptilolite from Wyoming, described as mordenite, is entirely different in habit, forming thin tabular crystals, like those of heulandite. Pirsson's analysis agrees closely with the formula for ptilolite, the ratios of SiO₂:Al₂O₃:(Ca, Na₂, K₂)O:H₂O being 10.10:1.04:1.05:6.78. The refractive indices, determined on part of the original material, kindly supplied by Professor W. E. Ford from the Brush collection, are given below.

OPTICAL PROPERTIES

The determinations of the optical properties of mordenite, and ptilolite, as given in the literature, may be brought together in the following two tables, extending the data given by Ross and Shannon.

OPTICAL PROPERTIES OF MORDENITE

Locality	α	β	γ	Sign	Extinction
Idaho	1.475	1.477	1.478
Idaho (1)	1.470	1.475	1.475	—	$X \wedge c = 3^\circ 40'$, $Z = b$
Idaho (2)	1.472	1.475	1.476	Small
Idaho (3)	1.473
Idaho (4)	1.473
Nova Scotia (How)	1.473	Small
Nova Scotia (Walker and Parsons)	1.471	1.475	Small
Iceland	1.472	1.474	—	5°
Average	1.472	1.474	1.476	About 5°

OPTICAL PROPERTIES OF PTILOLITE

Locality	α	β	γ	Sign	Extinction
Colorado	1.476	1.480	1.480	—	0°
Utah	1.473	1.475	1.478	0°
Elba	1.480	1.482	—	0°
Iceland	1.480	0°
Average	1.474	1.478	1.480	0°

Clinoptilolite is optically negative. Z to a -axis is 15° , whence Y to c -axis = $16\frac{1}{2}^\circ$, according to Pirsson. Crushed fragments show extinction angles of about 34° . Larsen determined α as 1.476 and γ as 1.479; $2V$ very small, dispersion $\rho < \nu$ strong. Cleavage $b(010)$, nearly $\perp Y$.

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MIX-CRYSTALS OF Ca_2SiO_4 AND Mn_2SiO_4 *

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INTRODUCTION

Former investigators have suggested that Ca_2SiO_4 (shannonite) and Mn_2SiO_4 (tephroite) are isomorphous, but little optical and no x-ray data have been obtained to support this view. The present writer has prepared a series of artificial minerals containing measured proportions of Ca_2SiO_4 and Mn_2SiO_4 and subjected the series to optical and x-ray study. The work was aided by many valuable suggestions and criticisms offered by Dr. A. N. Winchell. Thanks are also due Dr. R. C. Emmons for assistance in the use of the high temperature equipment and double variation apparatus required in attacking the problem.

HISTORICAL REVIEW

Both end members of the series were prepared years ago, but it was not until 1914 that St. Kallenberg¹ synthesized a series of melts containing various proportions of Ca_2SiO_4 and Mn_2SiO_4 . More recently Tokody² published an account of a similar research. Both investigators concluded, on the basis of fusion temperatures, densities, molecular weights, and molecular volumes, that Mn_2SiO_4 is isomorphous with the γ -phase of Ca_2SiO_4 . Day and Shepherd³ have shown that Ca_2SiO_4 exists in three phases, viz., the α -phase, stable only above 1410°C ., the β -phase, stable between 1410° and 675°C ., and the γ -phase, which exists below 675°C . A 10 per cent volume increase occurs when inversion to the γ -phase takes place. Wright⁴ states that the α -phase is monoclinic, the β -phase orthorhombic, and the γ -phase probably monoclinic.

THE SERIES IN NATURE

Mn_2SiO_4 is represented in nature by the rare mineral tephroite. Glaucochroite, corresponding to CaMnSiO_4 , is found at the same

* A brief form of a thesis submitted to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

¹ St. Kallenberg: *Zeits. f. Anorg. Chemie*, **88**, (1914), pp. 355-359.

² L. Tokody: *Zeits. f. Anorg. Chemie*, **169**, (1928), pp. 51-56.

³ A. L. Day and E. S. Shepherd, with optical study by F. E. Wright: *Am. Jour. Sci.*, **22**, (1906), pp. 265-302.

⁴ *Op. cit.*

locality, i.e., Franklin, N. J. The lime orthosilicate is exceedingly rare, but the β -phase has been reported from Tasmania⁵ and Quebec.⁶

PROCEDURE

Melts containing MnO are difficult to produce since this substance takes on more oxygen very readily at temperatures well below its fusion point. Previous workers have overcome this difficulty by heating in a stream of nitrogen. This practice was not feasible in the present investigation: instead, heating was carried on in a vacuum, an electric furnace devised by R. C. Emmons⁷ being used. In this furnace a strong electric current is passed through a pair of carbon electrodes, one being hollow and functioning as a crucible.

Molecular proportions of ordinary C.P. quality CaCO_3 , MnCO_3 and SiO_2 were carefully weighed, mixed, and packed into the crucible which is approximately 1 inch long and 1/8 inch in diameter. Before heating was commenced the air in the furnace was evacuated. A temperature of 800–1000°C. was maintained for a few moments to drive off the CO_2 . The carbon electrodes and transite framework of the furnace contain much absorbed air, which is given off as the temperature rises. For this reason the air pump was kept in operation during the entire procedure. When the sintering was complete the current was increased until the temperature exceeded the theoretical melting point by 50–100°C. The current was then decreased slowly. Since MnO oxidizes so readily and a little air is always being given off from the electrodes and the transite framework, cooling is allowed to proceed rapidly, seldom for more than five minutes. The crystals so formed were small, but optical data could usually be obtained from them with accuracy. Not infrequently strain effects precluded precise orientation. The crystals were then heated for approximately 10 minutes at a temperature not more than 200° below their melting point. This operation eliminated the strain effects and caused crystal enlargement. In the case of the lime-rich melts such procedure was found inadvisable for two reasons. In the first place the melting temperatures are so high that air was released more abundantly from the system and combined more readily with the MnO. Secondly, the MnO con-

⁵ F. P. Paul: *Tsch. Min. Pet. Mit.*, **25**, (1906), p. 309.

⁶ N. L. Bowen: *Am. Jour. Sci.*, **3**, (1922), p. 30.

⁷ R. C. Emmons: *Science*, **73**, (1931), pp. 499–500.

tent of these mixtures was so small that a very small amount of air was sufficient to convert it entirely to MnO_2 .

DESCRIPTION OF THE ARTIFICIAL CRYSTALS

Tephroite is greyish and glaucocroite bluish-green, but all of the artificial minerals which contain 30 per cent or more of Mn_2SiO_4 are marked by a decided greenish coloration. With less Mn_2SiO_4 the crystals crumble to a white powder. Tokody suggests that the crumbling is due to the 10 per cent volume increase which $\beta\text{-Ca}_2\text{SiO}_4$ undergoes when inverting to the stable γ -phase. In thin section the crystals are colorless to light-brown and show high relief. Tiny dark inclusions are common in the manganese-rich minerals. Their identity was not determined. Possibly they are hausmannite which forms readily when MnO is oxidized.

OPTICAL STUDIES

The optical work consisted chiefly in obtaining three indices of refraction and the optic angle for crystals of each melt. The double variation method of R. C. Emmons⁸ was used in conjunction with a Leitz universal stage modified by Emmons.⁹ An error of $\pm .0005$ for the refractive indices, and 2° to 3° for the observed optic angle may be expected in sodium light; indices are accurate to $\pm .001$ for other wavelengths. For indices up to 1.74 the liquids recommended by Emmons were used. By dissolving sulphur in methylene iodide a maximum of 1.79 could be obtained. The further addition of iodoform brought the liquid to 1.83.

The results (see Table 1 and Fig. 1) show a progressive and rather regular decrease in indices of refraction from 100 per cent Mn_2SiO_4 to 100 per cent Ca_2SiO_4 (Wright's¹⁰ figures for $\gamma\text{-Ca}_2\text{SiO}_4$ have been used.) Apparently there is no regular change in the optic angle. Mn_2SiO_4 is orthorhombic and might be expected to be isomorphous with the orthorhombic $\beta\text{-Ca}_2\text{SiO}_4$. This does not appear to be the case for the indices of $\beta\text{-Ca}_2\text{SiO}_4$ are definitely higher than those of any melt containing less than 60 per cent Mn_2SiO_4 . Furthermore, the optical character of $\beta\text{-Ca}_2\text{SiO}_4$ is positive, whereas the optic sign is negative in all the preparations studied by the writer. It appears inescapable that it is the *supposedly* monoclinic

⁸ R. C. Emmons: *Am. Min.*, **13**, (1928), pp. 504-515. *Am. Min.*, **14**, (1929), pp. 414-426

⁹ R. C. Emmons: *Am. Min.*, **14**, (1929), pp. 441-461.

¹⁰ F. E. Wright: *Op. cil.*

γ - Ca_2SiO_4 which is isomorphous with Mn_2SiO_4 . The evidence for placing γ - Ca_2SiO_4 in the monoclinic system is admittedly weak. Wright's indices are those of a positive mineral, whereas he states that the optic sign is negative. The limits of error stated for the indices are sufficient however to account for this discrepancy.

TABLE I

Comp.		N_g	N_m	N_p	$N_g - N_p$	2V Calc.	2V Obs.	Pleochroism
100% Mn_2SiO_4	F	1.8369	1.8258	1.7920	.0449	60° 30'		X = Brown
	D	1.8143	1.8038	1.7720	.0423	61° 20'	60°	Y = Brownish-red
	C	1.8102	1.7997	1.7681	.0421	60° 15'		Z = Blue
80% Mn_2SiO_4 20% Ca_2SiO_4	F	1.7854	1.7750	1.7415	.0439	58° 40'		X = Brown
	D	1.7717	1.7592	1.7257	.0460	62° 40'	59°	Y = Brownish-red
	C	1.7678	1.7547	1.7206	.0472	64°		Z = Blue
70% Mn_2SiO_4 30% Ca_2SiO_4	F	1.7685	1.7594	1.7335	.0350	60° 30'		X = Brown
	D	1.7570	1.7463	1.7180	.0390	63°	not obs.	Y = Brownish-red
	C	1.7538	1.7428	1.7138	.0400	64°		Z = Blue
60% Mn_2SiO_4 40% Ca_2SiO_4	F	1.7518	1.7460	1.7212	.0306	53°		X = Brown
	D	1.7352	1.7248	1.6980	.0372	64°	not obs.	Y = Brownish-red
	C	1.7304	1.7196	1.6917	.0387	65°		Z = Blue
50% Mn_2SiO_4 50% Ca_2SiO_4	F	1.7342	1.7253	1.7010	.0332	62°		X = Pale Brown
	D	1.7205	1.7105	1.6850	.0355	64°	67°	Y = Pale Brown
	C	1.7178	1.7072	1.6810	.0368	65°		Z = Pale Bluish
40% Mn_2SiO_4 60% Ca_2SiO_4	F	1.7166	1.7076	1.6930	.0236	76°		Not observed
	D	1.6998	1.6945	1.6798	.0200	62°	not obs.	
	C	1.6979	1.6928	1.6780	.0199	60°		
30% Mn_2SiO_4 70% Ca_2SiO_4	F	1.6992	1.6954	1.6878	.0114	64°		X = Pale Brown
	D	1.6842	1.6800	1.6704	.0138	68°	not obs.	Y = Pale Brown
	C	1.6802	1.6759	1.6647	.0155	64°		Z = Faint Blue
20% Mn_2SiO_4 80% Ca_2SiO_4	F	1.6874	1.6843	1.6797	.0077	79°		Not Observed
	D	1.6747	1.6714	1.6638	.0109	64°	not obs.	
	C	1.6705	1.6671	1.6598	.0107	65°		
10% Mn_2SiO_4 90% Ca_2SiO_4	F	1.6738	1.6730	1.6633	.0105	22° (?)		X = Pale Brown
	D	1.6607	1.6580	1.6505	.0102	62°	62°	Y = Pale Brown
	C	1.6584	1.6549	1.6475	.0109	67°		Z = Colorless

Unfortunately the reaction $\text{CaO} + 3\text{C} = \text{CaC}_2 + \text{CO}$ commences at 1620°C. whereas the fusion point of γ - Ca_2SiO_4 is about 2080°. Accordingly this mineral cannot be synthesized in a carbon crucible. Day and Shepherd¹¹ state that γ - Ca_2SiO_4 can be prepared in platinum, but the equipment necessary was not available to the writer.

¹¹ *Op. Cit.*, p. 280.

It was therefore impossible to check the optical and crystallographic data on the lime end-member. It would be extremely desirable to do this.

X-RAY STUDIES

To throw more light on the problem x-ray powder photographs of the series were made. It will be noted (see plate 1) that the pat-

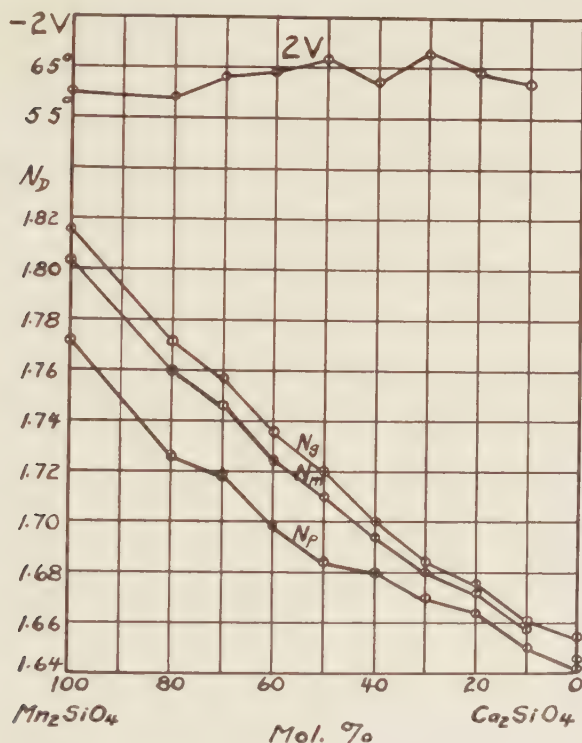


Fig. 1. Variation in Refractive Indices and Optic Angle.

terns of natural and artificial tephroite are identical except that the entire pattern of the former is offset to the left with respect to that of the latter. An inspection of all of the photographs indicates that the amount of offsetting is a function of the amount of non-manganese content. Natural and artificial glaucocroite display interesting similarities. The patterns of the minerals containing between 100 and 50 per cent Mn_2SiO_4 are in excellent accord. The

PLATE I. X-RAY PATTERNS OF THE $\text{Ca}_2\text{SiO}_4\text{-Mn}_2\text{SiO}_4$ SERIES% Ca_2SiO_4 % Mn_2SiO_4

0

100 (Approx.)
Nat. Tephroite

0

100
Art. Tephroite

10

90

30

70

40

60

50

50
Art. Glaucochroite

50

50
Nat. Glaucochroite

60

40

70

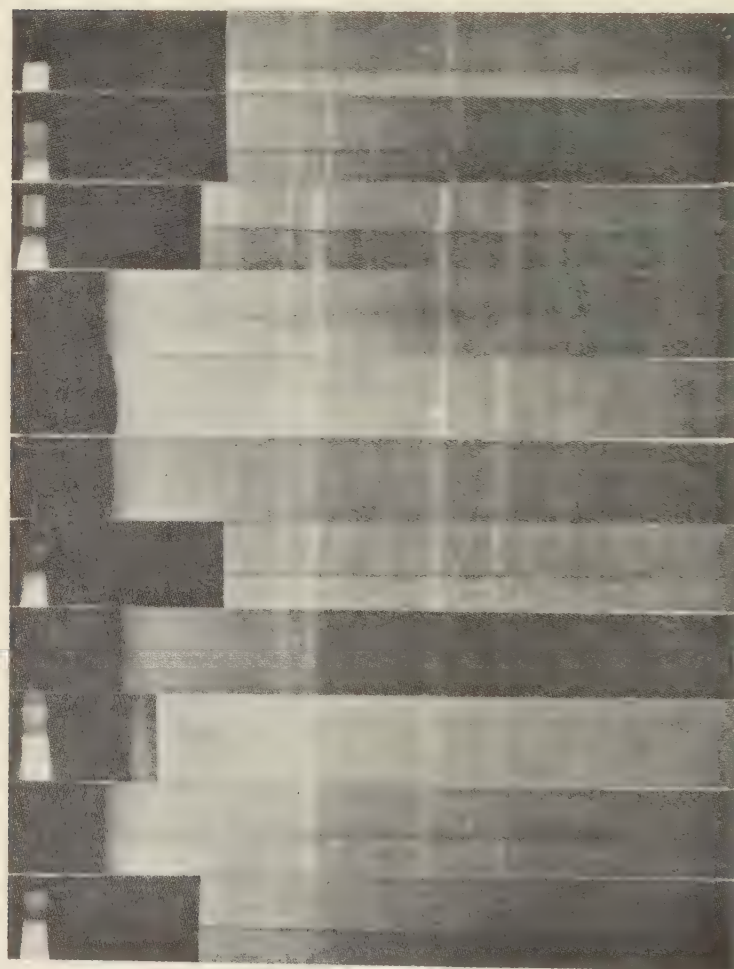
30

80

20

90

10



patterns of the lime-rich varieties, while similar in that the principal lines are offset to the left, also show some lines which do not correspond with any in the patterns of the manganese-rich minerals. Considerable difficulty was encountered with the 50, 60, and 70 per cent Ca_2SiO_4 minerals. The first photographs obtained from them showed a number of rather faint lines which failed to check with those of the high-manganese types. Practically every line of the manganese-rich minerals was represented more or less distinctly however. Accordingly, three new mixtures were prepared and photographed. The resultant patterns of the 50 and 70 per cent Ca_2SiO_4 minerals were then found to fit much better, but that of the mineral containing 60 per cent Ca_2SiO_4 was still anomalous. Next, four minerals, all containing 60 per cent Ca_2SiO_4 —40 per cent Mn_2SiO_4 were synthesized, two being sintered at 1100°C . for 10 minutes after fusion, the other pair not so treated. Both of the former gave more satisfactory patterns, while both of the latter yielded anomalous results. Comparison under the microscope was then made. The product which had been sintered proved to be made up of crystals showing good extinction. The unsintered product showed a few grains which could be oriented on the universal stage and which yielded optical values very close to that of the sintered material. The remaining grains however were made up of a confused mass of tiny crystals on which no accurate optical study could be made. Nevertheless it was possible to determine that the refractive indices of this material are probably not far removed from those of the sintered mineral.

The reason for the anomalous behavior of the lime-rich species is not clear. The x -ray evidence seems to indicate that two substances are present in some of the unsintered material and only one in the sintered variety. The inference is that sintering changes one of the substances to the other and since there is no evidence of chemical change the process must be that of inversion. Considering that pure Ca_2SiO_4 exists in three phases such inversion is not untoward.

CONCLUSIONS

1. Optical data appear to indicate that Mn_2SiO_4 and γ - Ca_2SiO_4 form mix-crystals in all proportions.
2. X -ray evidence shows clearly that calcium may replace manganese at least up to 50 per cent in the orthosilicates. Replacement

to an even greater extent is indicated but not proved. The lime-rich members of the series probably crystallize in two forms one of which can invert to the other.

3. Manganese and calcium may proxy for one another, at least at high temperatures, more completely than has been suspected previously.

4. It has generally been held that two substances belonging to different crystal systems cannot form an isomorphous series. It will be necessary to prove definitely that $\gamma\text{-Ca}_2\text{SiO}_4$ is monoclinic before concluding that a broader conception of isomorphism is required to explain the results obtained by the writer.

AN X-RAY STUDY OF PSILOMELANE AND WAD

LEWIS S. RAMSDELL, *University of Michigan.*

Ordinarily the identity of a mineral is established by means of either its crystallographic constants, its optical properties, its chemical composition, or some combination of these. In the case of psilomelane none of these means is sufficient. Psilomelane has never been found in crystals, it is opaque, and the variations in chemical analyses have made it impossible to even assign a formula to it.

The recognition of psilomelane as an independent mineral species depends, to a large extent, upon its possession of a certain combination of physical properties which have been regarded as characteristic. The name psilomelane means "smooth black," and refers to the black color and the smooth rounded surfaces resulting from its frequent occurrence in botryoidal, reniform or stalactitic forms. The hardness is 5-6, the streak black, and the smooth fracture usually reveals a dense fine-grained texture with no definite structure other than an occasional concentric banding.

In the absence of definite crystallographic, optical and chemical data, there are two other means available of defining more specifically the material called psilomelane. One of these is a mineragraphic examination, the other involves the use of x -rays. Both of these methods were used by Smitheringale¹ in a study of manganese minerals, which incidentally included two specimens of psilomelane. An etching test² has recently been described for distinguishing psilomelane from certain associated minerals in polished sections. However, none of these investigators had in mind the purpose of establishing the identity of psilomelane as an independent mineral species, and did not touch upon this phase of the subject.

This present investigation has been limited to the x -ray method, and represents an attempt to answer this question of whether or not the material commonly called psilomelane is in reality a definite mineral. The x -ray diffraction patterns obtained by the powder method are especially useful in such a case as this, for if psilomelane is a definite crystalline substance, it must have a characteristic pattern.

Approximately fifty specimens of material, coming from widely scattered localities, and all having to a greater or less extent those

¹ W. V. Smitheringale: *Econ. Geol.*, **24**, (1929), 481-505.

² S. R. B. Cooke, Warren Howes and A. H. Emery: *Am. Mineral.*, **16**, (1931), 209-212.

physical properties which are considered typical of psilomelane, have been photographed. There were also included specimens of the closely related material known as wad. In addition, for comparison purposes, powder photographs have been obtained from pyrolusite, polianite, manganosite, bixbyite, braunite, manganite, and hausmannite.

Each of the last named minerals has its own characteristic *x*-ray pattern, and can be identified readily by this means. But in the case of psilomelane, instead of a single characteristic pattern, a variety of patterns was obtained. In the group of specimens examined, three distinct crystalline types were observed, as well as a semi-amorphous type. The preponderance of the crystalline type is interesting, in view of the many references to psilomelane as an amorphous mineral. In the specimens of wad there was less evidence of crystallinity. Most of the patterns were poorly developed and indicated impure material of a colloidal nature. Such patterns as were observed were rather variable.

The first conclusion to be drawn from the *x*-ray evidence is that psilomelane is a blanket term, and includes a group of substances with more or less similar physical properties. A second conclusion which was made evident is that the physical properties of psilomelane, even considered as a group, are not distinctive. There is so much overlapping of properties that they alone are insufficient for identification. For example, some specimens which had the normal appearance of psilomelane were found to be pyrolusite or braunite. On the other hand, some which had little or no resemblance to psilomelane, actually proved to be psilomelane.

Since psilomelane has never been precisely defined, in this paper the name has arbitrarily been assigned to the type of material which was most abundant among the specimens studied. This distinction cannot be made on the basis of physical properties, for no consistent difference could be found between these specimens and the others. Its identification is based solely on the diffraction pattern, which is shown in Fig. 1a. To avoid confusion in this paper, this material will be referred to as "true" psilomelane.

For the purposes of description the specimens which were included in this study can be divided into three groups, on the basis of their *x*-ray patterns.

GROUP 1

The specimens in this group include the majority of the specimens examined, and represent the material arbitrarily considered as "true" psilomelane. Although they vary considerably in detailed characteristics, all have in common the black color, hardness, and fine even-grained texture, which have been considered typical of psilomelane, and most of them are botryoidal. These specimens are from widely scattered localities, including Bohemia, Hungary, Saxony, Nova Scotia, Vermont, N. Carolina, Wisconsin and Michigan, as well as several specimens from unknown localities.

GROUP 2

Here are included those specimens whose patterns are different from that of "true" psilomelane, yet which in the past have been identified as psilomelane. First there is a group of five specimens which gave the type of diffraction pattern shown in Fig. 1 b. The localities and brief descriptions of these specimens are as follows: Laramie Co., Wyoming, stalactitic (labelled "manganese fulgerite"); Knapp's Ranch, Calif., rough granular crust; Romanèche, France, smooth botryoidal crust, with radial fibrous structure; two specimens from unknown localities, one with a smooth botryoidal crust, composed of distinct concentric layers; the other a thin dense crust.

Dana lists a psilomelane from Romanèche, France, with a BaO content of 16 per cent. This suggested that the above specimen from the same locality might contain barium. Accordingly it was tested, and considerable barium found. The remaining four specimens were likewise found to contain barium. Five specimens taken at random from Group 1 gave negative results when tested for this element. Definite analyses of these specimens should be made, but the preliminary qualitative results strongly suggest that the so-called psilomelane with an appreciable barium content is in reality a distinct mineral.

In addition to these Ba-containing specimens, there were two specimens labelled "psilomelane, variety lithiophorite," one from Saxony and one from Silesia. It is perhaps doubtful as to whether this material should have been classed as a variety of psilomelane. In appearance it is identical with ordinary psilomelane, but it is softer, and it is supposed to contain lithium and aluminum. No analyses were made, but the diffraction pattern, shown in Fig. 1c,

is distinctly different from that of "true" psilomelane, showing that here too, we are dealing with a distinct crystalline substance. A specimen labelled "psilomelane, variety Kakochlor," also from Silesia, was photographed. Breithaupt used this name for a variety of asbolite. This particular specimen, however, is similar in appearance to the two lithiophorite specimens, and gave an identical diffraction pattern.

Finally, in this group of specimens which have the appearance of psilomelane, but which differ from "true" psilomelane, there are included several specimens which have been designated as semi-amorphous. Powder photographs of extremely fine crystalline material are characterized by diffuse patterns, with relatively few lines. Patterns of this type were secured from some of the psilomelane specimens. In some cases there was partial agreement of the few lines present with the more intense lines of the true psilomelane pattern while in others there was little agreement, and it is doubtful as to whether they represent a minutely crystalline phase of psilomelane or something else. Such material is probably colloidal, and may be rather indefinite in composition. These specimens do not show any consistent differences in appearance from the true psilomelane.

GROUP 3

In this group are included those specimens which possess the characteristic appearance of psilomelane, but which proved to be either pyrolusite or braunite. Ordinarily pyrolusite and psilomelane are regarded as so distinctly different in physical properties that there would be little possibility of confusing the two. Yet these specimens were found, having the botryoidal structure and hardness of psilomelane, and not distinguishable in appearance from the specimens of group 1, but which give the pyrolusite pattern. The occurrence of pyrolusite with a hardness of 6 is not entirely unexpected, for the mineral polianite, considered as a modification of MnO_2 , occurring in tetragonal crystals, has a hardness of 6 to 6.5. This was shown by St. John³ to have a structure identical with pyrolusite, and this has been verified in this present study. Apparently the relation of polianite to pyrolusite is similar to that of hematite crystals to the softer varieties such as red ocher. In this case we might expect to find MnO_2 with any hardness from 1 to

³ A. St. John: *Phys. Rev.*, **21**, (1923), 389.

6.5. A specimen from an unknown locality was actually found, with the typical acicular structure of pyrolusite, which had a hardness of about 3.5.

A specimen supposed to be psilomelane, from Santa Clara, Calif., gave the braunite pattern. This specimen is not botryoidal, but it is dense and fine grained, with an even fracture, and would normally

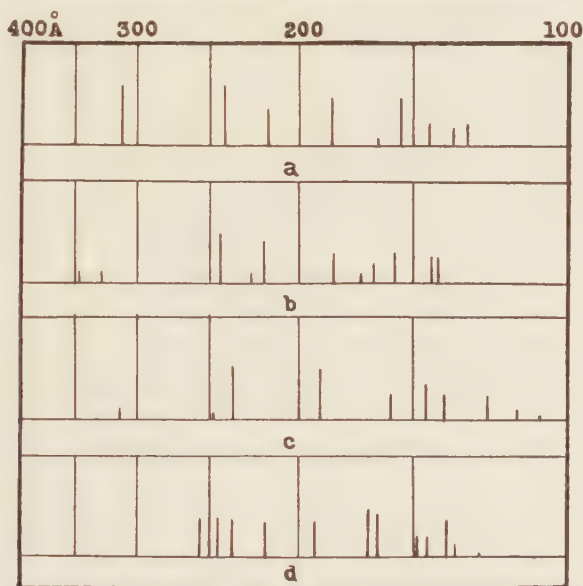


FIG. 1. X-ray diffraction patterns of (a) "true" psilomelane, (b) psilomelane containing barium, (c) lithiophorite, and (d) possible dimorphous form of MnO_2 .

be identified as psilomelane on the basis of its appearance. Two additional specimens, one from Sheffield, Mass., and the other from Eagle Harbor, Mich., also proved to be braunite. Both were labelled psilomelane, but they have a cellular structure, and would not be classed as having the typical appearance of psilomelane. Braunite was also found as a granular crust on pyrolusite. These specimens indicate that the occurrence of massive braunite may be more common than has been believed.

WAD

No x-ray evidence was obtained to indicate the existence of any definite mineral which could be called wad. The x-ray patterns re-

vealed that much of the so-called wad is either pyrolusite or true psilomelane, while the rest consists of impure material of a semi-amorphous character.

A specimen from Spain, gray brown in color, soft, earthy, and almost light enough to float on water; together with a very similar material, occurring as a soft brown coating on botryoidal psilomelane from Hurley, Wis., both gave distinct patterns identical with that of "true" psilomelane. On the other hand, a specimen from China,⁴ almost indistinguishable from the one from Spain, proved to be practically amorphous.

The soft sooty material frequently associated with pyrolusite was in some cases found to be pyrolusite and in others true psilomelane, but in no case was it amorphous. There was nothing in the appearance of the specimens to give any indication as to which of the two was actually present.

UNUSUAL SPECIMENS

Two of the specimens which were studied seem worthy of special description. The first, from Nassau, Germany, is steel gray in color, and possesses a distinctly radial fibrous structure. Not only is the specimen fibrous, but in places this structure grades into distinct individual needles, which project several millimeters from the surface. Both the needles and the fibrous portion give the "true" psilomelane pattern. The second specimen, from an unknown locality, is soft and black, and to a certain extent resembles ordinary pyrolusite. However, there is a parallel grouping of the needles which gives an almost platy appearance. The x-ray pattern, shown in Fig. 1d, is entirely different from anything else obtained in this investigation. But after heating to a low dull red heat, a normal pyrolusite pattern was secured. This heating was accompanied by a loss of water of only 1 per cent, and the total loss in weight was less than 2 per cent. This would seem to eliminate either dehydration or a change from some other oxide as a cause of the change in pattern. A possible explanation is that this specimen represents an unstable form of MnO_2 , which is converted to the normal form by heating.

⁴ Collected by F. L. Hess, and made available to the writer through the kindness of E. P. Henderson.

SUMMARY

1. X-ray examination of over fifty specimens of psilomelane shows that material included under this name may be any one of several different substances. The term "true" psilomelane has arbitrarily been applied to the type of material which was most abundant among the specimens studied. No identification of "true" psilomelane is possible by means of physical properties alone.

2. Material which in the past has been classified as psilomelane may actually be:

a. "True" psilomelane.

b. Pyrolusite or braunite.

c. A distinct mineral, which has been previously considered as psilomelane containing barium.

d. Lithiophorite, previously considered as a variety of psilomelane containing lithium and aluminum, but which the x-ray pattern shows to be a distinct mineral.

e. Semi-amorphous material, which probably can best be classed as wad, but which shows no consistent difference in appearance from true psilomelane.

3. Material which has been classed as wad may actually be:

a. Pyrolusite.

b. "True" psilomelane.

c. Impure material, of semi-amorphous character.

AUTHIGENIC TOURMALINE IN THE ORISKANY SANDSTONE

MARCELLUS H. STOW, *Cornell University.*

During the course of a detailed petrographic investigation of the Oriskany Sandstone of Virginia, West Virginia, Maryland, Pennsylvania, and New York, well rounded detrital grains of tourmaline with a jagged secondary growth were discovered. Careful microscopic examination has proved this secondary material to be authigenic tourmaline.

The growth in question is nearly colorless, but usually has a slight tinge of the same color as the parent grain. The secondary portion of the grain has parallel crystallographic orientation with the tourmaline to which it is attached, as evidenced by simultaneous extinction and identical position of maximum absorption. On one

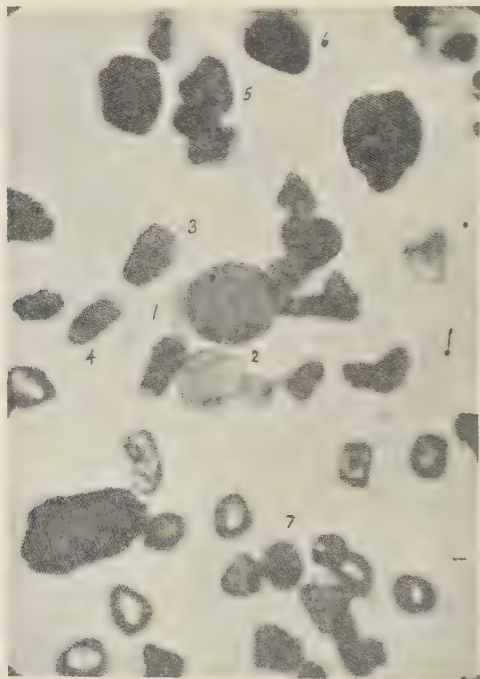


FIG. 1. Authigenic Tourmaline on Detrital Tourmaline (numbered grains), Zircon (other non-opaque grains), and Limonite (irregular opaque grains). Arrow Indicates Vibration Direction in Lower Nicol. Magnification 42 \times . From Warm Springs, Virginia.

fragment a negative uniaxial interference figure was obtained.

The appearance and abundance of the enlarged grains are shown in the accompanying photographs of a part of the heavy separate of a specimen from Warm Springs, Virginia. In figure 1 not less than seven secondarily enlarged tourmalines may be seen. The exposure was taken with a magnification of 42 diameters and with only one nicol prism. Zircons and irregular lumps of limonite may also be recognized. Figure 2 shows the two central grains of figure

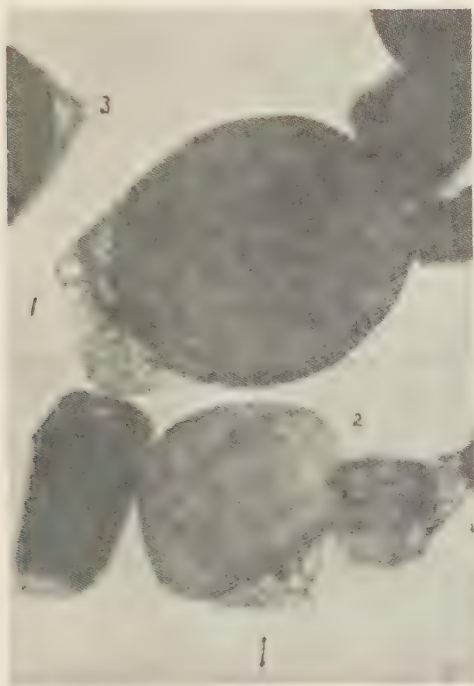


FIG. 2. Center of Fig. 1. Magnified 134 \times .

1 magnified 134 diameters. In it there appears very clearly the character of the secondary material and the sharp boundary between it and the well rounded, darker colored, detrital grain. In the larger of these two grains, the "c" crystallographic axis is parallel to the elongation of the grain, and in the smaller it is at right angles to it. However, in each case the secondary material is attached at the end of the "c" axis regardless of the elongation. Furthermore, the secondary material is on only one end, or side,

of the grain. This is true, without exception, of all the grains on which this growth was observed, raising interesting speculation as to the possible connection between the polarity of tourmaline structure and its enlargement.

When these grains were first found it was thought that the secondary material was formed under local conditions at that particular place. However, as the study of the slides progressed it became evident that these occurred at so many localities throughout the entire area that purely local conditions could not be assigned for their origin. The splintery character is certain evidence that it could not have been attached to the original tourmaline grains before transportation as it would necessarily have been broken off. It must have grown after the original grains had come to rest.

The authigenic tourmaline shown in the photomicrographs is typical of that found throughout the Oriskany. It was seen in seventy-four of one hundred and sixteen heavy mineral slides, representing thirty of the seventy localities studied. Following is a list of the localities at which this unusual tourmaline was found in the Oriskany.

Virginia: Monterey, Pinckney, Wilsonville, Cleeks Mills, Warm Springs, Bath Alum Springs, Millboro Springs, Goshen, Straitcreek, Stack Mines. West Virginia: Franklin, Smoke Hole, Sweet Springs, Gap Mills, Ridgeley, Berkeley Springs, Capon Bridge, Hanging Rock Gap. Maryland: Tonoloway Ridge. Pennsylvania: Experiment Mills, Lewistown, Mill Creek, Huntingdon, Everett, Hyndman, Warren Point. New York: Union Springs, Aurelius, Skaneateles Falls, Oriskany Falls.

Just what light this secondary growth of tourmaline may throw on the physical and chemical conditions which have existed in the Oriskany formation is not yet clear. At this time no attempt has been made to study the phenomenon in detail and no explanation of its origin is attempted.

The only other occurrence of authigenic tourmaline of which the writer is aware is described in an article by H. Wichman¹ who bases his conclusion that the tourmaline is authigenic on the fact that it is found in very perfect crystals. This is in marked contrast with the splintery development of the tourmaline growths in the Oriskany.

¹ Wichman, H., Tourmaline as an Authigenic Constituent of Sands; *Neues Jahrb.*, II, pp. 294-297, 1888.

DETRITAL COLLOPHANE

JAMES H. C. MARTENS, *West Virginia University.*

A few years ago Professor A. F. Rogers¹ wrote a paper entitled "Collophane, a Much Neglected Mineral," showing that collophane deserved recognition as a valid mineral species, and that considering it as an appendix to apatite was unjustified and the attention devoted to it was inadequate. Collophane is well known as the principal mineral of many of the economically valuable phosphate deposits, as well as in nodules, concretions, etc., in various sediments in which it is not concentrated enough to be of any commercial value. It has long been recognized that in the land and river pebble phosphate deposits of Florida,² and in the river phosphate deposits of South Carolina,³ the phosphate pebbles and grains were mostly derived from an older formation, a phosphatic marl, in which the collophane was presumably an authigenic constituent. *Detrital* collophane, outside of the workable pebble phosphate deposits, does not appear to have received much notice. Cayeux⁴ described the different modes of occurrence of phosphate of lime in sediments, but made definite mention of a detrital origin only in the case of apatite. Milner⁵ mentions briefly some of the occurrences of detrital collophane described in this paper.

The purpose of the present note is to describe collophane as it occurs in sand grains and to point out the fairly wide distribution of collophane in this form, especially in the coastal plain deposits of the southeastern states.

Collophane sand grains are generally well rounded and have smooth polished surfaces. The size of the grains varies from a few hundredths of a millimeter upward, and naturally varies with the coarseness of the sand in which they occur. The color is brown, gray or black by reflected light. According to A. F. Rogers⁶ the specific gravity of collophane is from 2.6 to 2.9, the hardness from 3 to 5, and the index of refraction from about 1.57 to 1.63. The higher figure for specific gravity applies more nearly to the collophane

¹ *Am. Journ. of Science*, 5th series, vol. 3, pp. 269-276, 1922.

² Sellards, E. H., *Florida State Geological Survey*, 7th Annual Report, pp. 25-116, 1915.

³ Rogers, G. S., *U. S. G. S.*, Bull. 580, pp. 183-220, 1915.

⁴ Cayeux, Lucien, *Etude Petrographique des Roches Sedimentaire*, pp. 234-241.

⁵ Milner, H. B., *Sedimentary Petrography*, Second Edition, 1929, p. 260.

⁶ *Am. Journ. of Science*, 5th series, vol. 3, p. 275, 1922.

occurring in sand studied by the writer, since most of the collophane grains sink in bromoform of specific gravity 2.85. Under the microscope, by transmitted light, the color is yellow to brown. The coloring matter is not uniformly distributed, and a large proportion of it, if not all, is in the form of small dark inclusions which are probably some kind of carbonaceous material. These frequently render the centers of the grains nearly opaque. Small inclusions of calcite and somewhat larger ones of quartz were noticed in a few instances but do not seem to be common.

Collophane in small grains is optically isotropic. Collophane grains in beach sand from one locality on South Carolina, two in Georgia, and three in Florida all have their refractive indices between 1.600 and 1.615. Considering the amorphous nature of the mineral its index seems very uniform, although it is likely that the examination of a larger number of grains and material from more localities would show a greater variation.

Collophane does not closely resemble any other mineral likely to occur in sands, but as an additional check qualitative chemical tests for phosphate were made on a few selected grains, and these tests gave positive results. On account of its easy solubility collophane is not found in sands which have been treated with acid.

The known occurrences of collophane in the beach sand of the Atlantic coast extend from Charleston, South Carolina, south to Miami, Florida. The approximate localities at which sands containing collophane were collected are as follows:

SOUTH CAROLINA	GEORGIA	FLORIDA
Folly Beach, near Charleston	Tybee	Amelia Island
	St. Simon Island	Mineral City
		St. Augustine
		Daytona Beach
		Indianalantic Beach
		Hollywood
		Miami

It is probable that collophane occurs at all of the intervening localities along this coastal beach since it was not found to be absent from any of the samples in which search was made for it. The actual proportion of collophane present, referred to the whole sand, is not very great, but it may make up as much as ten percent of the heavy minerals separated by bromoform. The amount is greatest near Charleston, somewhat less near Jacksonville, Florida, and becomes very small indeed on the east coast of southern Florida.

For a few miles on the southwest coast of Florida collophane is one of the principal minerals in the beach sand. At Venice the sand is nearly black from the abundance of dark grains of this mineral, which are derived from a sandy phosphatic limestone or limy sandstone outcropping at this locality. A grain count on a sample in which the heavy minerals had been somewhat concentrated by wave action gave: quartz 41.5%, collophane 36.0%, shell fragments 2.3%, with various heavy minerals making up the remainder.

Detrital collophane, as pebbles and grains, occurs in recent alluvial deposits in the rivers and smaller streams at many localities in various parts of Florida and around Charleston, South Carolina.⁷ It is by no means limited to deposits which have been worked for river pebble phosphate, but is much more widespread in its occurrence. The above mentioned land pebble phosphates of Florida contain collophane, which is principally of detrital origin, as the valuable mineral, and rolled grains and pebbles of collophane occur frequently in Florida in other Pliocene and Pleistocene sediments in which the percentage of phosphate is too low, or on which the overburden is too great for them to be worked as phosphate rock.

G. M. Ponton⁸ of the Florida State Geological Survey, reports that collophane, apparently detrital, occurs in well samples of the later Tertiary formations from many localities in Florida.

Phosphatic marl of Miocene age is the original source of the detrital phosphate grains in South Carolina, Georgia and Florida. The phosphate-bearing formation is known as the Edisto marl in South Carolina⁹ and the Hawthorn formation in Florida.¹⁰ The immediate source of some of the collophane in recent deposits is Pliocene and Pleistocene sediments containing collophane which had previously been derived from the Miocene phosphatic marl.

Considering its softness and comparatively easy solubility, it is not to be supposed that collophane in appreciable quantity could survive either transportation over a long distance or weathering through a long period of time, but as shown by the occurrences in the southeastern states, it may occur rather abundantly as a detrital mineral where source beds are near at hand and weathering has not been too thorough.

⁷ Rogers, G. S., *U. S. G. S.*, Bull. 580, pp. 183-220, 1915.

⁸ Personal communication, Aug. 29, 1931.

⁹ Rogers, G. S., *U. S. G. S.*, Bull. 580, pp. 183-222, 1915.

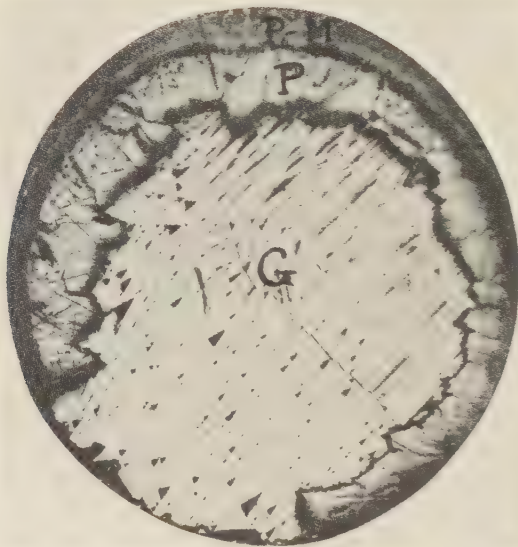
¹⁰ Cooke, C. Wythe and Mossom, Stuart, *Florida State Geological Survey*, 20th Annual Rept., pp. 115-137, 1929.

NOTES AND NEWS

GALENA REPLACING PENNSYLVANIAN ROOTLET*

VICTOR T. ALLEN, *Saint Louis University.*

While collecting clays for petrographic examination under the auspices of the Illinois State Geological Survey, the underclay of Coal No. 2 near Dayton, LaSalle County, Illinois, was visited with Mr. J. E. Lamar. Near the center of the NW $\frac{1}{4}$ S32 T34N R4E the writer observed in the underclay a small cylindrical mass of iron sulphide surrounding a core of galena. In outward appearance it is similar to the rods of pyrite or marcasite which are frequently seen replacing plant rootlets in the clays below Illinois coals. This occurrence of galena, however, seems sufficiently unique to merit a brief description.



SULPHIDES REPLACING PENNSYLVANIAN ROOTLET IN ILLINOIS UNDERCLAY. $\times 10$.

P-M. Pyrite and marcasite retaining cell structure and forming a complete circle which is only partially included in the photomicrograph.

P. Pyrite with small areas of calcite near the contact with galena.

G. Galena forming inner core.

The polished surface of this specimen (shown in the accompanying figure) contains four minerals, pyrite, marcasite, galena and

* Published with the permission of the Chief, Illinois State Geological Survey.

calcite. The outermost ring is composed mainly of fine grained pyrite and forms a complete circle. Small patches have a paler color and these when examined in polarized reflected light are anisotropic, indicating marcasite rather than pyrite. Cell structure of the rootlet is retained in these sulphides and presumably the outer part was more fibrous and better suited to replacement and preservation than the pulpy interior. Its circular form suggests that replacement of the outer part took place before the rootlet was flattened or crushed. Coarser crystalline pyrite lines the interior almost three-fourths of the way around the circumference which is dotted by two or three small patches of calcite. The galena completely fills the inner core and it may have replaced some of the coarser grained pyrite. It was probably introduced somewhat later than the other minerals for its contact with the pyrite is sharp.

This occurrence records the deposition of galena in north central Illinois in post Lower Pennsylvanian time. The galena was deposited by cold waters, for the adjacent clay minerals have the same optical properties as the areas remote from the galena and are identical to the typical Illinois underclay.

PROCEDURE FOR RESTANDARDIZING CLERICI'S SOLUTION

HAROLD H. HAWKINS, *University of Kansas*.

In 1929, Dr. Kenneth K. Landes¹ prepared a set of heavy liquids to be used in specific gravity determinations. One year later he rechecked these liquids and found that they did not vary sufficiently to be restandardized. Now, two years after the original preparation, the specific gravities have been found to differ sufficiently from the desired gravities to require restandardization. The change in gravity has in every instance been an increase, due to the evaporation of water from the solutions. In restandardizing the specific gravity set originally prepared by Landes the writer developed a method that not only saves time, but gives results more accurate than are actually required. For practical use no solution should vary in specific gravity more than 0.015 from its intended gravity, that is, it should be between 1.985 and 2.015 for an intended gravity of 2.0. In the following procedure, which was used in restandardizing twenty-two different solutions, the variation

¹ Landes, K. K., Rapid specific gravity determinations with Clerici's solution: *American Mineralogist*, vol. 15, pp. 159-162, April, 1930.

between the solution obtained and the desired specific gravity was in the third decimal place, thus giving a far greater accuracy than required. By the use of this procedure a second or "check" weighing can be eliminated.

APPARATUS NEEDED

- 1 Special Westphal balance, with plummet sufficiently heavy to be used in liquids with a specific gravity as high as 4.2.
- 1 Separatory funnel or dropper (10–12 drops per cubic centimeter is convenient).
- 1 Graduate cylinder (graduated for $\frac{1}{2}$ cubic centimeter).

PROCEDURE

With the Westphal balance determine the specific gravity of the solution to be restandardized. Then measure the volume of *all* the liquid to be restandardized in the graduated cylinder. Multiply this volume by the specific gravity. The result is the total specific weight of the solution. The information now needed is the volume of distilled water that must be added to the solution of known specific weight in order to dilute it to the desired specific gravity. A simple proportion may be set up with two unknowns, X and Y . That is, if X is the amount of distilled water that is to be added, Y is the total volume of solution that will be obtained. But because Y is not desired the equation may be solved for X only, by the use of simultaneous equations. X will then be the number of cubic centimeters of distilled water that must be added. Frequently this figure is less than one cubic centimeter. Therefore, it is better to calculate in terms of drops rather than in cubic centimeters. This may be done by calibrating a funnel containing a valve or a medicine dropper. Time will be saved if the number of drops to each cubic centimeter range between ten and twelve. The number of drops of distilled water may now be easily calculated. The water should be dropped directly into the solution in the graduated cylinder. Because Clerici's solution is miscible in all proportions in water it can be mixed by either shaking or stirring. The specific gravity of the final solution will be well within the allowable error.

EXAMPLE

Specific gravity of solution = 2.2574

Total volume to be restandardized = 12.5 c.c.

Desired specific gravity of solution = 2.0

$$12.5 (2.2574) + X = 2Y$$

$$\begin{array}{r} 12.5 \qquad \qquad + X = Y \\ \hline \end{array}$$

$$X = 3.22$$

Number of drops of distilled water in 1 c.c. = 11.3

$$3.22(11.3) = 36.4$$

Add to original solution 36 drops of distilled water.

CHECK

By determining again with the Westphal balance

Specific gravity = 2.0015

Error = 2.0015 - 2.0000 = 0.0015

Allowable error = 0.015

Dr. Waldemar T. Schaller of the U. S. Geological Survey delivered three lectures before the students of Columbia University on February 15, 16 and 17. The subjects discussed were: The Potash Deposits of New Mexico and Texas; Borate Deposits in the Southwest; and Crystal Cavities in the New Jersey Zeolite Region.

Dr. Charles H. Richardson, professor of mineralogy and head of the department at Syracuse University for more than twenty-five years, has been appointed director of the Natural Science Museum. He has been relieved of a large part of the teaching duties so as to have time for research and museum work.

The eighth meeting of the Mineralogical Society of Southern California was held in the Lecture Hall of the Pasadena Public Library on Feb. 8, 1932. Mr. David B. Scott, manager of the Natural Soda Products Company at Keeler, Inyo County, was the speaker on this occasion.

PROCEEDINGS OF SOCIETIES

MINERALOGICAL SOCIETY OF GREAT BRITAIN AND IRELAND
MINERALOGICAL SOCIETY, *Tuesday, January 19.* Sir John S. Flett, President, in the chair.

DR. L. J. SPENCER: *A new pallasite from Alice Springs, Central Australia.* A fragment weighing 1084 grams was collected by Dr. Herbert Basedow in 1924 on the north side of the MacDonnell Ranges about ten miles north of Alice Springs, and has been generously presented by him to the British Museum collection of meteor-

ites. It is a typical pallasite consisting of 40 per cent of olivine (with $\text{FeO}:\text{MgO} = 4.6$) and 60 per cent of nickel-iron ($\text{Fe}:\text{Ni} = 12.7$) with a little troilite. Small angular fragments of olivine are embedded in the kamacite, suggesting that the olivine had been broken up before the kamacite crystallized out. The granular texture of the metal also suggests that the kamacite had been broken up with the development of Neumann lines before the separation of the taenite and plessite, and that the fragments had been partly redissolved in the residual melt, giving the reaction rim of taenite. Finally, the plessite eutectic separated out in the small interspaces.

ARTHUR RUSSELL: *An account of British mineral collectors and dealers in the seventeenth, eighteenth, and nineteenth centuries.* (contd.) Short biographies dealing with Robert Were Fox, (1789–1877), Wilson Lowry, (1762–1824), and Thomas Hogg.

M. H. HEY: *Studies on the zeolites, Part III, Natrolite and metanatrolite.* Natrolite is shown by nine new analyses and new x-ray measurements to have a constant Si/Al-ratio and a unit-cell formula of $\text{Na}_{16}\text{Al}_6\text{Si}_{24}\text{O}_{80} \cdot 16\text{H}_2\text{O}$, in agreement with previous results. $\text{Na}_2 \rightarrow \text{Ca}$ replacement may occur up to about 4, and $\text{Na} \rightarrow \text{K}$ replacement up to about 2 atoms per unit-cell. Natural etch-figures in natrolite from Benallt, Carnarvonshire (a new locality for natrolite), show the symmetry to be didigonal polar (C_{2v}). A detailed study of the optical properties of natrolite has been made. Some observations have been made on the effects of partial dehydration on the optical properties. The vapour-pressure has been studied at various temperatures and degrees of dehydration, and a discontinuity in physical properties at a water content of 15 mols. per unit-cell observed. Some experiments have been carried out on the base-exchange of natrolite. Optical and x-ray examination of metanatrolite have been made.